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For: METHODS FOR FORMING RUTHENIUM FILMS WITH β-DIKETONE CONTAINING
        RUTHENIUM COMPLEXES AND METHOD FOR MANUFACTURING METAL-
        INSULATOR-METAL CAPACITOR USING THE SAME

Commissioner for Patents
P.O. Box 1450
Alexandria, Va. 22313-1450

STATEMENT OF ACCURACY OF A TRANSLATION
37 CFR 1.52(d), 37 CFR 1.55(a) AND 37 CFR 1.69

I, the below named translator, hereby state that:

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That I am knowledgeable in the English language and in the language of the

[ ] attached document

[X] below identified document

and I believe the attached English translation to be a true and complete translation of this document.

The Certified Copy of the Korean priority application:
2003-12044, filed February 26, 2003

[X]   This foreign language document was filed in the USPTO on September 8, 2003.

17 June 2005
Date

Soon-hee Lee
Full name of the translator

Signature of the translator

Post Office Address: _284 Hagye-dong, Nowon-gu,_

Seoul, Korea

ABSTRACT

[Abstract of the Disclosure]

Provided are a method for forming a ruthenium film under a single process condition, whereby high adhesion of the ruthenium film to a lower layer is maintained, and a method for manufacturing an metal-insulator-metal (MIM) capacitor using the ruthenium film forming method. The method for forming a ruthenium film includes supplying bis(isoheptane-2,4-dionato)norbornadiene ruthenium at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm, and depositing the ruthenium film at a temperature of 330-430°C under a pressure of 0.5-5 Torr using chemical vapor deposition (CVD).

[Representative Drawing]

FIG. 2

[Key Words]

Bis(isoheptane-2,4-dionato)norbornadiene ruthenium

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S P E C I F I C A T I O N

[Title of the Invention]

Method for Forming Ruthenium Film and Method for Manufacturing Metal Insulator Metal Capacitor Using the Same

[Brief Description of the Drawings]

FIG. 1 is a general formula of a conventional ruthenium source for forming a ruthenium film.

FIG. 2 is a cross sectional view of a ruthenium film formed on a semiconductor substrate according to the present invention.

FIGS. 3 to 5 are formulas of ruthenium sources for forming ruthenium films according to embodiments of the present invention.

FIG. 6 is a graph showing variation in a deposition rate with temperature using a ruthenium source according to the present invention.

FIG. 7 is a graph showing variation in resistivity with temperature using a ruthenium source according to the present invention.

FIG. 8 is a graph showing variation in deposition rate with pressure using a ruthenium source according to the present invention.

FIG. 9 is a graph showing variation in resistivity with pressure using a ruthenium source according to the present invention.

FIG. 10 is a graph showing variation in each of resistivity, deposition rate, and step coverage with oxygen flow rate using a ruthenium source according to the present invention.

FIGS. 11A, 11B and 11C are photographs of ruthenium films formed at an oxygen flow rate of 16 sccm using a ruthenium source according to the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition.

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FIGS. 12A, 12B and 12C are photographs of ruthenium films formed at an oxygen flow rate of 40 sccm using a ruthenium source according to the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition.

FIGS. 13A, 13B and 13C are photographs of ruthenium films formed at an oxygen flow rate of 70 sccm using a ruthenium source according to the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition.

FIG. 14 is a graph showing variation in deposition rate with a flow rate of a ruthenium source according to the present invention.

FIG. 15 is a graph showing variation in resistivity with a flow rate of a ruthenium source according to the present invention.

FIG. 16 is a graph showing variation in leakage current density with applied voltage using a ruthenium source according to the present invention.

FIGS. 17A and 17B are cross sectional views of a semiconductor substrate in successive steps in a method for manufacturing a metal-insulator-metal (MIM) capacitor according to the present invention.

<Description of Reference Numerals for Main Components of Drawings>

100, 200: semiconductor substrate	110,220: ruthenium film
225: lower electrode	230: dielectric layer
235: upper electrode	240: capacitor

[Detailed Description of the Invention]

[Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to a method for forming a ruthenium film and a method for manufacturing a metal-insulator-metal (MIM) capacitor using the ruthenium film formation method. More particularly, the present invention relates a method for forming a ruthenium film under a single process condition, whereby high adhesion of the ruthenium film to a lower layer is maintained, and a method for manufacturing an MIM capacitor using the ruthenium film formation method.

Recently, due to excellent electric properties such as resistivity, ruthenium or ruthenium compounds are being used as thin film electrode materials in the production of semiconductor devices for Dynamic Random Access Memory (DRAM) and Ferroelectric Random Access Memory (FeRAM).

Ruthenium or ruthenium compound films are mainly formed by sputtering or chemical vapor deposition (CVD) methods. In particular, CVD is preferred since thin layers with uniform thickness are easily formed.

In order to form ruthenium films using CVD, a ruthenium source is required. Recently, bis(ethylcyclopentadienyl)ruthenium [$Ru(EtCp)_2$] as shown in FIG. 1 is mainly used as a ruthenium source. Such an organic ruthenium compound is obtained by replacing one hydrogen on each of two cyclopentadiene rings of bis(cyclopentadienyl)ruthenium with an ethyl group. Because the bis(ethylcyclopentadienyl)ruthenium has a low melting point, it is in a liquid state at room temperature. Therefore, the bis(ethylcyclopentadienyl)ruthenium has a good handling property.

However, the bis(ethylcyclopentadienyl)ruthenium has problems in its use as a material for a ruthenium film.

Basically, it is difficult to carry out nucleation of the bis(ethylcyclopentadienyl)ruthenium. In order to solve this problem, ruthenium films are generally formed under increased oxygen flow rate and deposition pressure. However, if the oxygen flow rate and the deposition pressure are increased, nucleation rate per unit area is excessively increased. As a result, ruthenium films are formed in a needle shape. Formation of such needle-shaped ruthenium films results in growth of a

surface morphology, increase of a sheet resistance, and generation of a leakage current.

On the other hand, if ruthenium films are formed under decreased deposition pressure and oxygen flow rate, a nucleation rate is excessively lowered. As a result, ruthenium grains are separated from each other.

For the forgoing reasons, in case of using the bis(ethylcyclopentadienyl)ruthenium as a ruthenium source for forming films, ruthenium films are formed using a method comprising (a) carrying out nucleation of the bis(ethylcyclopentadienyl)ruthenium under increased oxygen flow rate and deposition pressure and (b) depositing the ruthenium films under decreased oxygen rate and deposition pressure.

In this case, however, due to different process conditions, a process burden is increased.

In addition, in a case where the two steps are in-situ carried out, a process condition becomes unstable during transitional stage between the two steps. As a result, the reproducibility and reliability of the process are lowered.

On the other hand, in a case where the two steps are carried out in two separate chambers, a residue may be left on a surface of a wafer when the wafer is transferred from one chamber to the other. Also, when a gas for cooling the wafer is introduced into a chamber, the wafer is often displaced due to the change in pressure. As a result, ruthenium films on the wafer do not have uniform thickness.

Meanwhile, the bis(ethylcyclopentadienyl)ruthenium has another problem in that ruthenium films made of the bis(ethylcyclopentadienyl)ruthenium have relatively low adhesion to silicon dioxide films which are mainly used as interlayer insulating layers.

[Technical Goal of the Invention]

The present invention provides a method for forming a ruthenium film under a single process condition, whereby high adhesion of the ruthenium film to a lower layer is maintained.

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The present invention also provides a method for manufacturing a metal-insulator-metal (MIM) capacitor using the ruthenium film formation method.

[Structure and Operation of the Invention]

5   In accordance with an aspect of the present invention, there is provided a method for forming a ruthenium film, the method comprising supplying a two β-diketones-coordinated ruthenium organic matter as a ruthenium source and oxygen onto a substrate and depositing the ruthenium film using chemical vapor deposition (CVD).

10   According to another aspect of the present invention, there is provided a method for forming a ruthenium film, the method comprising supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source at a flow rate of 0.2 to 0.1 ccm, and oxygen at a flow rate of 20 to 60 sccm onto a substrate and depositing the ruthenium film using CVD.

15   According to specific embodiments of the present invention, the ruthenium source is a two β-diketones and one diene-coordinated ruthenium complex, as represented by the general formula 1:

Formula 1
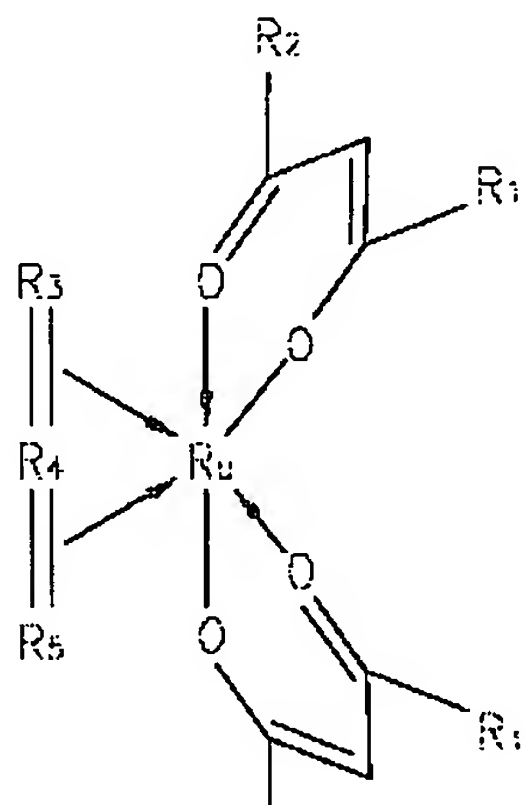
20   wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 3 to 5; and R_3, R_4 and R_5 are interconnected to each other to form a chain.

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The diene is 1,4-cyclohexadiene, norbornadiene, or 1,5-cyclooctadiene. Preferably, R_1 and R_2 are asymetric.

The ruthenium source is a two β-diketones and one diamine-coordinated ruthenium complex, as represented by the general formula 2:

Formula 2
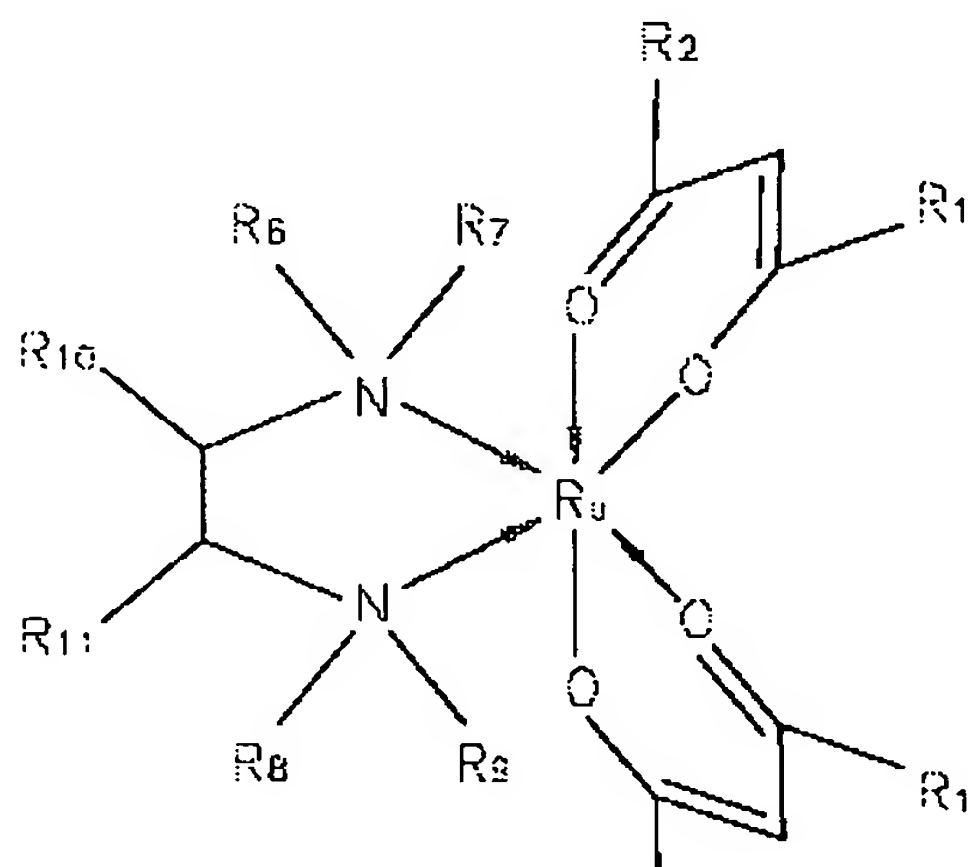
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 3 to 5; R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen or alkyl groups; and the total carbon number of R_6, R_7, R_8, R_9, R_{10} and R_{11} is 2 to 8.

The diamine is N,N,N',N'-tetramethylethylenediamine. Preferably, R_1 and R_2 are asymetric.

The ruthenium source is a two β-diketones and two organic ligands-coordinated ruthenium complex, as represented by the general formula 3:

Formula 3
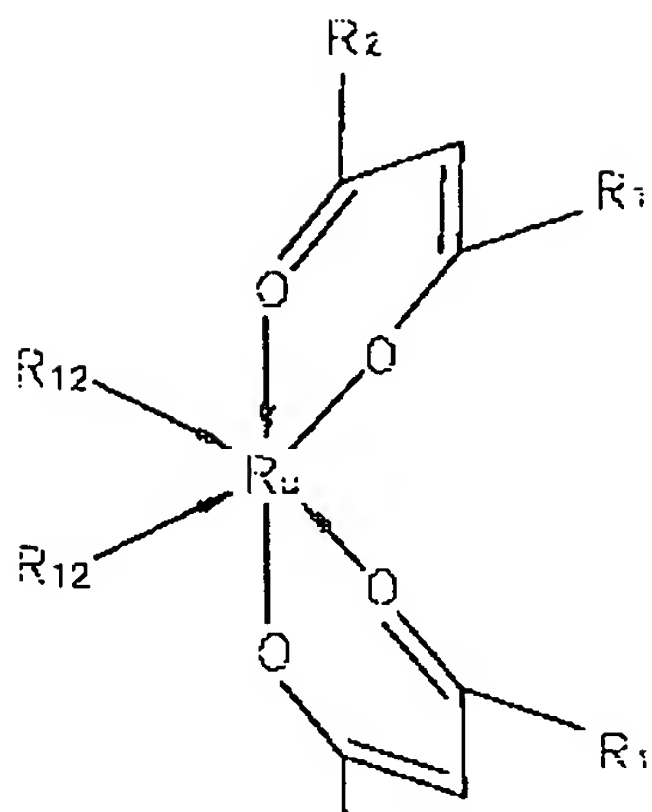
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; and two R_{12} groups are olefin, amine, nitrile or carbonyl.

As used as the organic ligand, the olefin is ethylene, propylene, 2-methylpropylene, butyl, or 1,3-butadiene; the amine is trimethylamine or triethylamine; and the nitirile is acetonitrile or acrylonitrile. The two β-diketones are 2,4-hexanedione, 5-methyl-2,4-hexanedione, 2,4-heptanedione, 5-methyl-2,4-heptanedione, 6-methyl-2,4-heptanedione, or 2,4-octanedione.

The ruthenium source are bis(isoheptane-2,4-dinato)norbornadiene ruthenium.

The ruthenium film is deposited at a temperature of 330-430℃ under a pressure of 0.5-5 Torr. When the ruthenium film is deposited, an inert gas such as nitrogen and argon is supplied onto the substrate.

According to another aspect of the present invention, there is provided a method for forming a ruthenium film, the method supplying bis(isoheptane-2,4-dionato)norbornadiene ruthenium as a ruthenium source at a flow rate of 0.2 to 1 ccm and oxygen at a flow rate of 20 to 60 sccm onto a substrate and depositing the ruthenium film using CVD at a temperature of 330-430℃ under a pressure of 0.5-5 Torr.

According to yet another aspect of the present invention, there is provided a method for manufacturing an MIM capacitor, the method comprising (a) forming a first ruthenium film for a lower electrode on a semiconductor substrate; (b) forming a

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dielectric layer on the lower electrode; and (c) forming a second ruthenium film for an upper electrode on the dielectric layer. Step (a) comprises supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm onto the substrate and depositing the first ruthenium film using CVD. Step (c) comprises supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm onto the substrate and depositing the second ruthenium film using CVD.

(Embodiments)

Hereinafter, exemplary embodiments of the present invention will be described with reference to the accompanying drawings. However, the present invention is not limited to these embodiments and various modifications can be carried out. The embodiments of the present invention are provided to assist ordinary persons skilled in the art in more clearly understanding the present invention. In this regard, each constitutional element on drawings is graphically expressed for proper understanding. The same numerals are used for the corresponding constitutional elements in drawings. As used herein, the expression "a first layer is formed "on" a second layer or a semiconductor substrate" include the case where the first layer indirectly contacts with the second layer due to a third layer between the first layer and the second layer, in addition to direct contact of the first layer and the second layer.

FIG. 2 is a cross sectional view of a ruthenium film formed on a semiconductor substrate according to the present invention. FIGS. 3 to 5 are formulas of ruthenium sources for forming ruthenium films according to embodiments of the present invention.

Referring to FIG. 2, first, a semiconductor substrate 100 is placed in a chamber. The substrate 100 may be a silicon substrate. A MOS transistor (not shown) and an interlayer insulating layer (not shown) may be formed on the substrate. Although not clearly shown in FIG. 2, a silicon dioxide film as an interlayer insulating layer is formed on the uppermost surface of the substrate 100. In accordance with the present

invention, a ruthenium film 110 is formed on the substrate 100 from a ruthenium source of the present invention using chemical vapor deposition (CVD).

In one embodiment of the present invention, a ruthenium source for forming the ruthenium film 110 is a two β-diketones and one diene-coordinated ruthenium complex (see FIG. 3). R_1 and R_2 as substituents of each β-diketone may be alkyl groups. The total carbon number of R_1 and R_2 is 3 to 5. Preferably, R_1 and R_2 may be asymetric. The diene may be 1,4-cyclohexadiene, norbornadiene or 1,5-cyclooctadiene.

In another embodiment of the present invention, a ruthenium source for forming the ruthenium film 110 is a two β-diketones and one diamine-coordinated ruthenium complex (see FIG. 4). R_1 and R_2 as substituents of each β-diketone may be alkyl groups. The total carbon number of R_1 and R_2 may be 2 to 5. Preferably, R_1 and R_2 may be asymetric. The two β-diketones may be 2,4-hexanedione, 5-methyl-2,4-hexanedione, 2,4-heptanedione, 5-methyl-2,4-heptanedione, 6-methyl-2,4-heptanedione, or 2,4-octanedione. R_6, R_7, R_8, R_9, R_{10} and R_{11} as substituents of the diamine are independently hydrogen or alkyl groups. Total carbon number of these substituents may be 2 to 8. The diamine may be N,N,N',N'-tetramethylethylenediamine.

In yet another embodiment of the present invention, a ruthenium source for forming the ruthenium film 110 is a two β-diketones and two organic ligands –coordinated ruthenium complex (see FIG. 5). R_1 and R_2 as substituents of each β-diketone may be alkyl groups. The total carbon number of R_1 and R_2 may be 2 to 5. Two R_{12} groups as the organic ligands are olefin, amine, nitrile or carbonyl. As used as the organic ligand, the olefin may be ethylene, propylene, 2-methylpropylene, butyl, or 1,3-butadiene; the amine may be trimethylamine or triethylamine; and the nitirile may be acetonitrile or acrylonitrile.

Hereinafter, optimal process condition for forming a ruthenium film will be described using bis(isoheptane-2,4-dionato)norbornadiene ruthenium

[Ru(C$_7$H$_8$)(C$_7$H$_{11}$O$_2$)$_2$, simply referred to as "bis norbornadiene ruthenium", hereinafter] as a ruthenium source.

In order to determine a relationship between a deposition rate and temperature, a deposition rate of a ruthenium film depending on temperature (330-440℃) was measured with varying a ruthenium source flow rate (0.2-1 ccm) and an oxygen flow rate (8-100 sccm). As shown in FIG. 6, a deposition rate showed little change over the temperature range when a ruthenium source flow rate and an oxygen flow rate were constant.

Under the same variable values as mentioned above, resistivity depending on temperature was measured with varying a ruthenium source flow rate and an oxygen flow rate. As shown in FIG. 7, it can be seen that resistivity does not depend on temperature when a ruthenium source flow rate and an oxygen flow rate are constant.

In order to determine a relationship between a deposition rate and pressure, a deposition rate of a ruthenium film depending on pressure (100-700 Torr) was measured with varying a ruthenium source flow rate (0.2-1 ccm) and an oxygen flow rate (8-100 sccm). As shown in FIG. 8, a deposition rate showed little change over the pressure range. Rather, a deposition rate was changed depending on a ruthenium source flow rate and an oxygen flow rate.

Under the same variable values as mentioned above, resistivity depending on pressure was measured with varying a ruthenium source flow rate and an oxygen flow rate. As shown in FIG. 9, pressure little affected resistivity.

Therefore, it can be said that temperature and pressure has minimal effects on the physical properties of ruthenium sources according to the present invention. However, with reference to a deposition temperature, ruthenium sources according to the present invention such as the bis norbornadiene ruthenium spontaneously decompose and react with other compounds at a temperature range of 250-500℃. Therefore, preferably, the film deposition is carried out at 250-500℃.

Next, resistivity, a deposition rate and step coverage were measured against varying an oxygen flow rate while the flow rate of a ruthenium source was kept constant.

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Oxygen was supplied with varying range of 0-100 sccm and a ruthenium source was supplied at a constant rate of 1 ccm. A deposition temperature was 350℃ and a deposition pressure was 1 Torr. In case of depositing a ruthenium film under the condition as mentioned above, as the oxygen flow rate was increased, resistivity was remarkably decreased but the deposition rate (deposition speed) was increased. Step coverage was gradually decreased after the oxygen flow rate exceeded 60 sccm.

FIGS. 11 to 13 show scanning electron microscope (SEM) photographs of ruthenium films of the present invention.

FIG. 11A, 11B and 11C represent photographs of ruthenium films formed at an oxygen flow rate of 16 sccm using a ruthenium source of the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition. FIGS. 12A, 12B and 12C represent photographs of ruthenium films formed at an oxygen flow rate of 40 sccm using a ruthenium source of the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition. FIGS. 13A, 13B and 13C represent photographs of ruthenium films formed at an oxygen flow rate of 70 sccm using a ruthenium source of the present invention; (A) a ruthenium film after deposition, (B) a ruthenium film that was annealed at 450℃ under a hydrogen atmosphere for 30 minutes after deposition, and (C) a ruthenium film that was annealed at 700℃ under a nitrogen atmosphere for 30 minutes after deposition.

As shown in FIGS. 11 to 13, when a ruthenium film is subjected to annealing at 450℃, a ruthenium source is sufficiently decomposed by the oxygen, resulting in reduction of impurities in the ruthenium film. In the ruthenium film surfaces from which impurities are removed, grain growth and agglomeration are partially caused. On the other hand, when a ruthenium film is annealed at 700℃, surface areas on which a small

amount of oxygen is provided have smooth surfaces. While, in surface areas on which a large amount of oxygen is provided, excess grain growth and agglomeration are caused (see FIG. 13C).

As apparent from the above description, in order to form a ruthenium film with optimal resistivity, deposition rate and step coverage, an oxygen flow rate is preferably 20 to 60 sccm.

Next, a deposition rate and resistivity will be described depending on a flow rate of ruthenium sources according to the present invention. FIG. 14 is a graph showing variation in deposition rate with a flow rate of a ruthenium source of the present invention. As shown in FIG. 14, a deposition rate is increased as a flow rate of a ruthenium source is increased. In particular, as both of an oxygen flow rate and a ruthenium source flow rate are increased, a deposition rate is remarkably increased.

Similarly, as the flow rate of a ruthenium source is increased, resistivity is increased (FIG. 15). However, resistivity is decreased as the oxygen flow rate is increased.

Therefore, in order to form a ruthenium film with optimal resistivity, deposition rate and step coverage, it is preferable to provide ruthenium sources of the present invention at a flow rate of about 0.2 to 1 ccm, and more preferably at 0.4 to 0.8 ccm.

In summary, the ruthenium film 110 with optimal resistivity, deposition rate, and step coverage according to the present invention can be formed under the following condition: an oxygen flow rate of 20 to 60 sccm, a ruthenium source flow rate of 0.2 to 1 ccm, a deposition temperature of 200 to 500°C, and preferably 330 to 430°C, a deposition pressure of 0.1 to 30 Torr, and preferably 0.5 to 5 Torr. Decomposition of a ruthenium source is maximally carried out at the aforementioned deposition temperature and pressure range.

Under the aforementioned condition, a ruthenium seed is uniformly distributed on the surface of an interlayer insulating layer and a high quality ruthenium film 110 is formed without altering the process condition. Furthermore, because the aforementioned two-step CVD process is not used, a process burden is reduced and

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device reliability is improved. In order to improve process efficiency, an inert gas such as nitrogen and argon may be supplied onto a substrate.

Meanwhile, adhesion of ruthenium films were tested using a ruthenium source of the present invention and the conventional bis(ethylcyclopentadienyl)ruthenium. The adhesion test refers to "peeling test". For the peeling test, ruthenium films were formed on wafers with a size of 20 cm x 20 cm. Each wafer was cut into total 1600 grids with a size of 5 mm x 5 mm as specimens. Then, cellophane tapes were attached to the specimens. After the cellophane tapes were removed from the specimens, the number of specimens that ruthenium films were peeled off from wafers was measured. In most specimens of the present invention, ruthenium films were not peeled off from wafers. However, in the conventional specimens, specimens that ruthenium films were peeled off from wafers totaled 35. Based on this test, it can be seen that ruthenium films formed using ruthenium sources of the present invention have superior adhesion to an interlayer insulating layer than those formed using a conventional ruthenium source.

FIG. 16 is a graph showing a leakage current density of a ruthenium film according to the present invention. It can be seen from FIG. 16 that ruthenium films of the present invention exhibit stable leakage current.

Hereinafter, a method for manufacturing an MIM capacitor using the aforementioned ruthenium film forming method will be described in detail.

Reference is made to FIG. 17A, an interlayer insulating layer 210 in which a storage node plug 205 is contained is formed on a semiconductor substrate 200. A mold oxide layer 215 is deposited on the interlayer insulating layer 210. An etch stopper (not shown) may be placed between the interlayer insulating layer 210 and the mold oxide layer 215.

Then, the mold oxide layer 215 is etched to expose the storage node plug 205, thereby forming a lower electrode area 218. A first ruthenium film 220 is formed on the mold oxide layer 215 and the lower electrode area 218. The first ruthenium film is formed by a method comprising supplying a ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 8-100 sccm and preferably 20-60 sccm onto a

substrate and depositing the ruthenium film at a temperature of 330-430℃ under a pressure of 0.5-5 Torr using CVD. The ruthenium source is a two β-diketones-coordinated ruthenium complex such as bis norbornadiene ruthenium. In case of using such a ruthenium source under the aforementioned single process condition, a ruthenium film with uniform thickness can be formed.

Reference is now made to FIG. 17B, the first ruthenium film 220 is subjected to chemical and mechanical polishing (CMP) to expose the mold oxide layer 215, resulting in formation of a lower electrode 225. Before the CMP process, a buffer oxide layer may be formed on the first ruthenium film 220. Then, the mold oxide layer 215 is removed in a conventional manner. Then, a dielectric layer 230, for example tantalum oxide layer (Ta_2O_5) is formed on the lower electrode 225 and the interlayer insulating layer 210. A second ruthenium film is formed on the dielectric layer 230 in the same manner as when forming the first ruthenium film 220 to thereby form an upper electrode 235. As a result, a capacitor 240 is produced.

Therefore, in case of manufacturing an MIM capacitor using the ruthenium film forming method of the present invention, a process step is simplified and excellent ruthenium electrodes can be obtained.

[Effect of the Invention]

As apparent from the above description, according to the ruthenium film forming method of the present invention, a ruthenium source is a two β-dikentones -coordinated ruthenium complex such as bis norbornadiene ruthenium. An oxygen flow rate, temperature, and pressure are optimally adjusted. Therefore, a ruthenium film which is excellent in resistivity, a deposition rate and step coverage is formed.

In addition, homogeneous nucleation occurs and a ruthenium film with uniform thickness is formed.

Furthermore, because a ruthenium film is formed under a single process condition, a process is simplified. As a result, process reproducibility and device reliability are improved. In addition, because vacuum is not generated during forming a

ruthenium film due to a constant pressure, a ruthenium film with uniform thickness is formed.

Still furthermore, ruthenium films formed using ruthenium sources of the present invention have excellent adhesion to an interlayer insulating layer. As a result, a leakage current that is caused by peeling of a ruthenium film from an interlayer insulating layer is prevented.

While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

What is claimed is:

1.   A method for forming a ruthenium film, the method comprising supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source and oxygen onto a substrate and depositing the ruthenium film using chemical vapor deposition

5   (CVD).

2.   The method according to claim 1, wherein the ruthenium source is a two β-diketones and one diene-coordinated ruthenium complex as represented by the formula 1:

(1)

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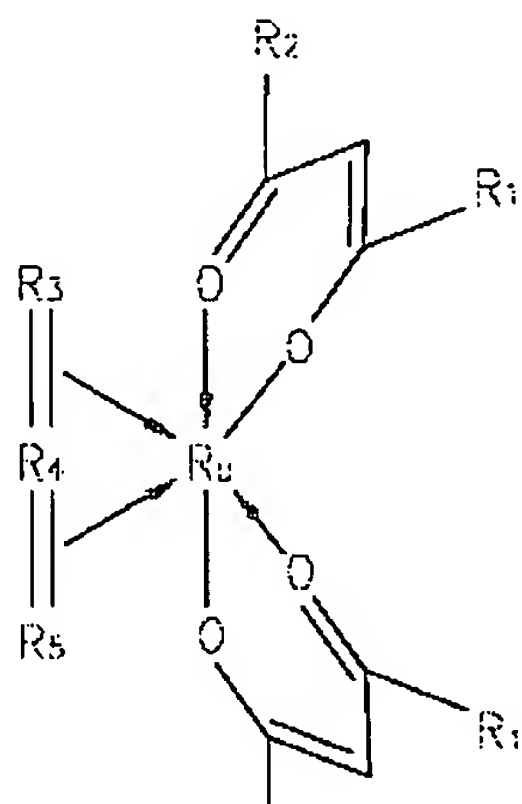
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 3 to 5; and R_3, R_4 and R_5 are interconnected to each other to form a chain.

15   3.   The method according to claim 2, wherein the diene is 1,4-cyclohexadiene, norbornadiene, or 1,5-cyclooctadiene.

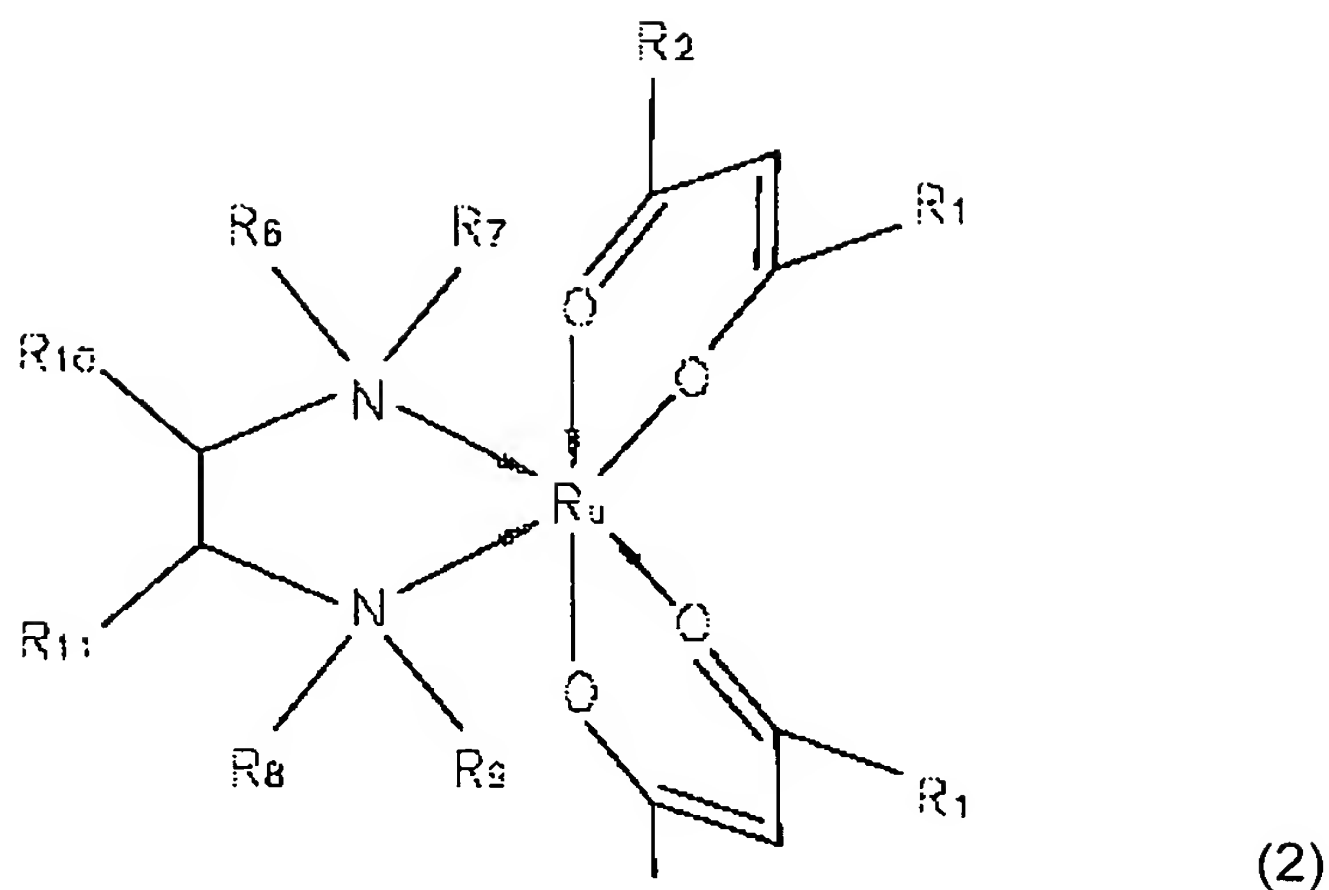4.   The method according to claim 2, wherein R_1 and R_2 are asymetric.

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5. The method according to claim 1, wherein the ruthenium source is a two β-diketones and one diamine-coordinated ruthenium complex as represented by the formula 2:

$$R_6 \quad R_7 \quad R_2 \quad R_1 \quad R_{10} \quad N \quad O \quad O \quad Ru \quad N \quad O \quad R_{11} \quad R_8 \quad R_9 \quad R_1$$

(2)
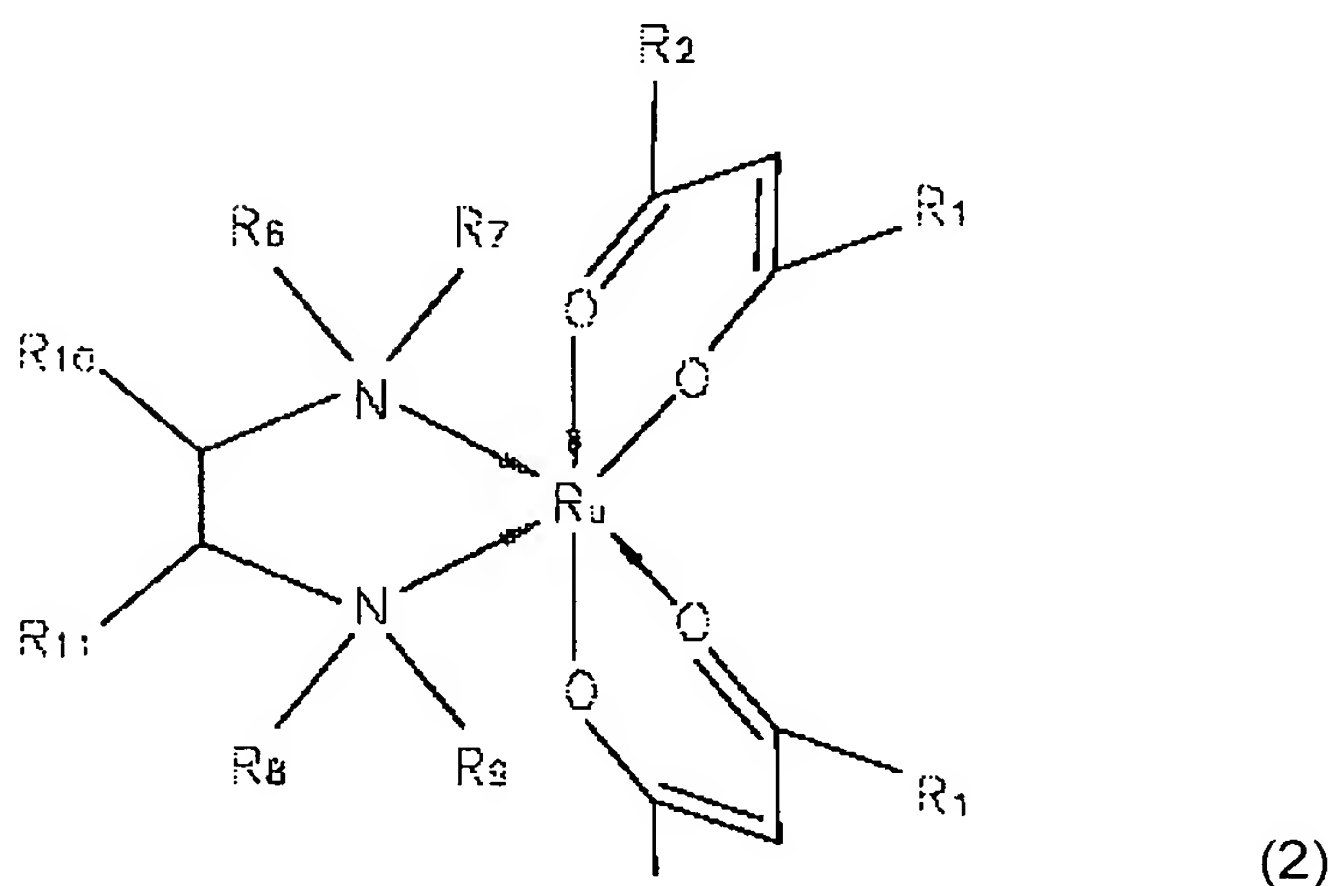
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen or alkyl groups; and the total carbon number of R_6, R_7, R_8, R_9, R_{10} and R_{11} is 2 to 8.
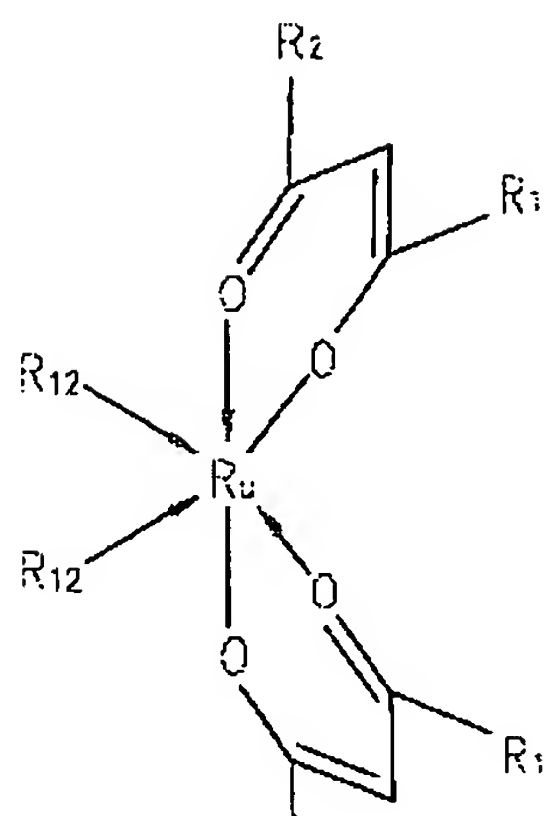
6. The method according to claim 5, wherein the diamine is N,N,N',N'-tetramethylethylenediamine.

7. The method according to claim 5, wherein R_1 and R_2 are asymetric.

8. The method according to claim 1, wherein the ruthenium source is a two β-diketones and two organic ligands-coordinated ruthenium complex as represented by the formula 3:

18

(3)
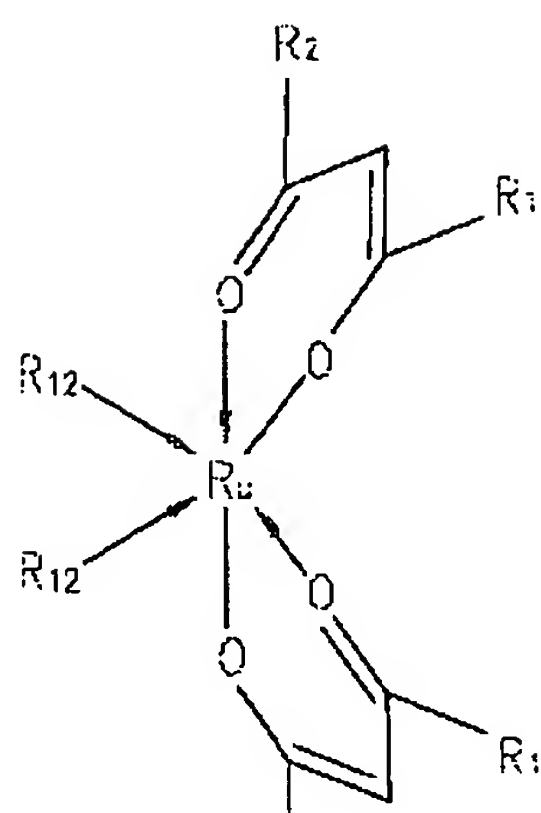
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; and two R_{12} groups are olefin, amine, nitrile or carbonyl.

9.　The method according to claim 8, wherein the olefin is ethylene, propylene, 2-methylpropylene, butyl, or 1,3-butadiene.

10.　The method according to claim 9, wherein the amine is trimethylamine or triethylamine.

11.　The method according to claim 10, wherein the nitirile is acetonitrile or acrylonitrile.

12.　The method according to claim 8, wherein the two β-diketones are 2,4-hexanedione, 5-methyl-2,4-hexanedione, 2,4-heptanedione, 5-methyl-2,4-heptanedione, 6-methyl-2,4-heptanedione, or 2,4-octanedione.

13.　The method according to claim 1, wherein the ruthenium source is bis(isoheptane-2,4-dionato)norbornadiene ruthenium ($Ru(C_7H_8)(C_7H_{11}O_2)_2$.

14.   The method according to claim 1, wherein the oxygen is supplied at a flow rate of 20-60 sccm.

15.   The method according to claim 14, wherein the ruthenium source is supplied at a flow rate of 0.2-1 ccm.

16.   The method according to claim 1, wherein the ruthenium film is deposited at a temperature of 330-430 ℃.

17.   The method according to claim 1, wherein the ruthenium film is deposited at a pressure of 0.5-5 Torr.

18.   The method according to claim 1, wherein the depositing of the ruthenium film includes supplying an inert gas including nitrogen and argon onto the substrate.

19.   A method for forming a ruthenium film, the method comprising supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm, and depositing the ruthenium film using CVD.

20.   The method according to claim 19, wherein the ruthenium source is a two β-diketones and one diene-coordinated ruthenium complex as represented by the formula 1:

(1)
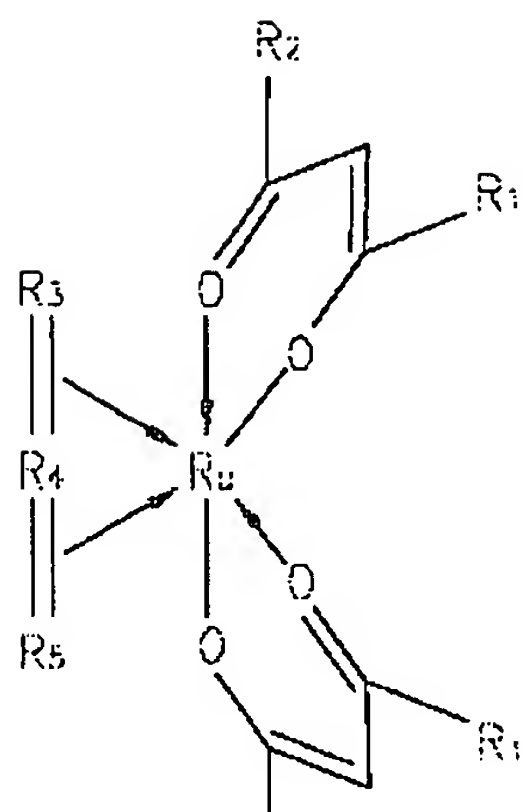
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 3 to 5; and R_3, R_4 and R_5 are interconnected to each other to form a chain.

5   21.   The method according to claim 20, wherein the diene is 1,4-cyclohexadiene, norbornadiene, or 1,5-cyclooctadiene.

22.   The method according to claim 20, wherein R_1 and R_2 are asymetric.

10   23.   The method according to claim 19, wherein the ruthenium source is a two β-diketones and one diamine-coordinated ruthenium complex as represented by the formula 2:

(2)

wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen or alkyl groups; and the total carbon number of R_6, R_7, R_8, R_9, R_{10} and R_{11} is 2 to 8.

5

24. The method according to claim 23, wherein the diamine is N,N,N',N'-tetramethylethylenediamine.

25. The method according to claim 23, wherein R_1 and R_2 are asymetric.

10

26. The method according to claim 19, wherein the ruthenium source is a two β-diketones and two organic ligands-coordinated ruthenium complex as represented by the formula 3:

(3)

wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; and two R_{12} groups are olefin, amine, nitrile or carbonyl.

27.   The method according to claim 26, wherein the olefin is ethylene, propylene, 2-methylpropylene, butyl, or 1,3-butadiene.

28.   The method according to claim 27, wherein the amine is trimethylamine or triethylamine.

29.   The method according to claim 28, wherein the nitirile is acetonitrile or acrylonitrile.

30.   The method according to claim 26, wherein the two β-diketones are 2,4-hexanedione,   5-methyl-2,4-hexanedione,   2,4-heptanedione, 5-methyl-2,4-heptanedione, 6-methyl-2,4-heptanedione, or 2,4-octanedione.

31.   The method according to claim 19, wherein the ruthenium source is bis(isoheptane-2,4-dionato)norbornadiene ruthenium.

32.   The method according to claim 19, wherein the ruthenium film is deposited at a temperature of 330-430°C.

33.   The method according to claim 19, wherein the ruthenium film is deposited under a pressure of 0.5-5 Torr.

34.   The method according to claim 19, wherein the depositing of the ruthenium film includes supplying an inert gas including nitrogen and argon onto the substrate.

35.   A method for forming a ruthenium film, the method comprising supplying bis(isoheptane-2,4-dionato)norbornadiene ruthenium at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm and depositing the ruthenium film at a temperature of 330-430°C under a pressure of 0.5-5 Torr using CVD.

36.   The method according to claim 35, wherein the depositing of the ruthenium film includes supplying an inert gas including nitrogen and argon onto the substrate.

37.   A method for manufacturing a metal-insulator-metal (MIM) capacitor, comprising:

(a) forming a first ruthenium film for a lower electrode on a semiconductor substrate;

(b) forming a dielectric layer on the lower electrode; and

(c) forming a second ruthenium film for an upper electrode on the dielectric layer,

step (a) comprising supplying a two β-diketones-coordinated ruthenium complex as a ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm onto the substrate and depositing the first ruthenium film using CVD, and step (c) comprising supplying a two β-diketones-coordinated ruthenium complex as a

ruthenium source at a flow rate of 0.2-1 ccm and oxygen at a flow rate of 20-60 sccm onto the substrate and depositing the second ruthenium film using CVD.

38.   The method according to claim 37, wherein the ruthenium source is a two β-diketones and one diene-coordinated ruthenium complex as represented by the formula 1:

(1)
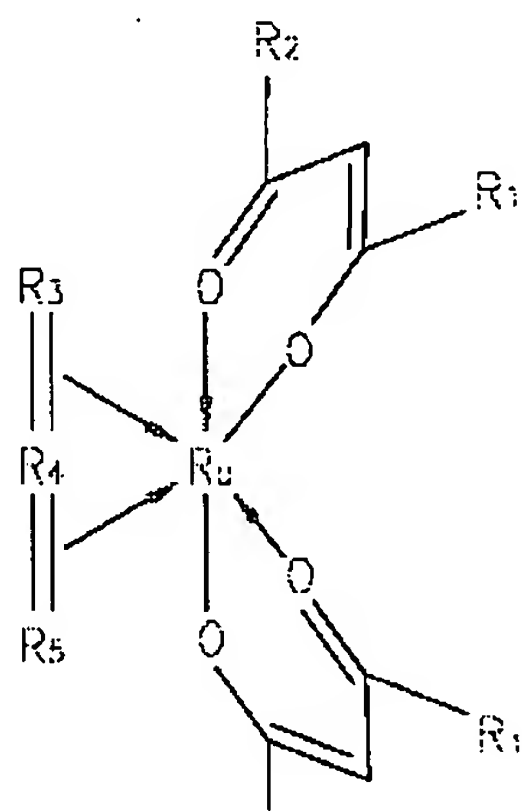
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 3 to 5; and R_3, R_4 and R_5 are interconnected to each other to form a chain.

39.   The method according to claim 38, wherein the diene is 1,4-cyclohexadiene, norbornadiene, or 1,5-cyclooctadiene.

40.   The method according to claim 38, wherein R_1 and R_2 are asymetric.

41.   The method according to claim 37, wherein the ruthenium source is a two β-diketones and one diamine-coordinated ruthenium complex as represented by the formula 2:

25

(2)
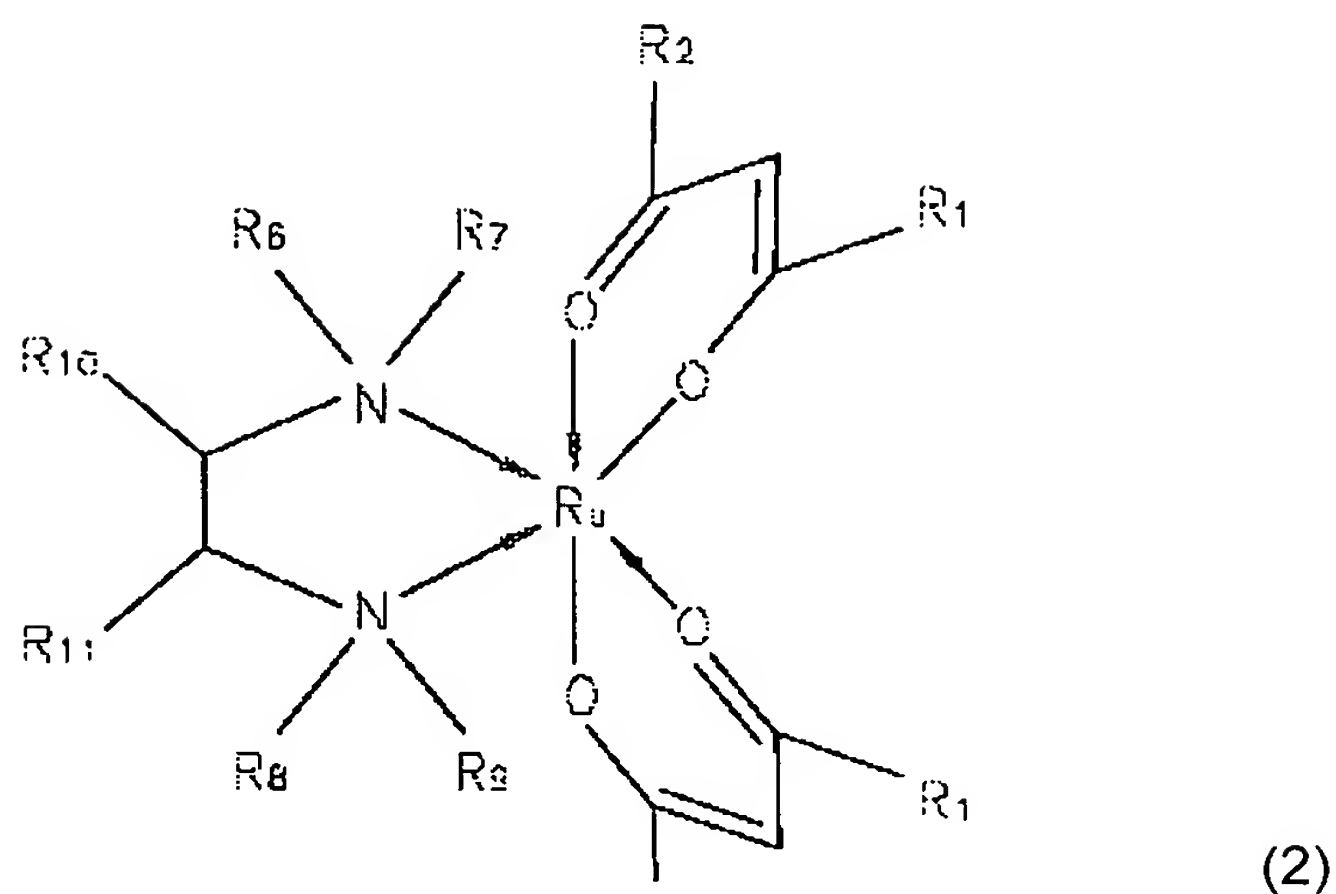
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen or alkyl groups; and the total carbon number of R_6, R_7, R_8, R_9, R_{10} and R_{11} is 2 to 8.

42.   The   method   according   to   claim   41,   wherein   the   diamine   is N,N,N',N'-tetramethylethylenediamine.

43.   The method according to claim 41, wherein R_1 and R_2 are asymetric.

44.   The method according to claim 37, wherein the ruthenium source is a two β-diketones and two organic ligands-coordinated ruthenium complex as represented by the formula 3:

(3)
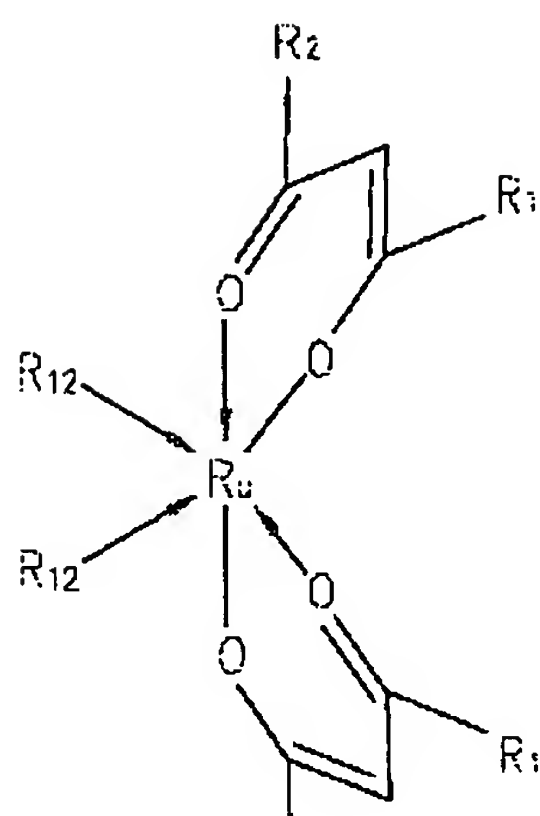
wherein, R_1 and R_2 are alkyl groups; the total carbon number of R_1 and R_2 is 2 to 5; and two R_{12} are olefin, amine, nitrile or carbonyl.

45.   The method according to claim 44, wherein the olefin is ethylene, propylene, 2-methylpropylene, butyl, or 1,3-butadiene.

46.   The method according to claim 45, wherein the amine is trimethylamine or triethylamine.

47.   The method according to claim 46, wherein the nitirile is acetonitrile or acrylonitrile.

48.   The method according to claim 45, wherein the two β-diketones are 2,4-hexanedione,   5-methyl-2,4-hexanedione,   2,4-heptanedione, 5-methyl-2,4-heptanedione, 6-methyl-2,4-heptanedione, or 2,4-octanedione.

49.   The method according to claim 37, wherein the ruthenium source is bis(isoheptane-2,4-dionato)norbornadiene ruthenium.

50.　The method according to claim 37, wherein the ruthenium film is deposited at a temperature of 330-430℃.

51.　The method according to claim 37, wherein the ruthenium film is deposited under a pressure of 0.5-5 Torr.

52.　The method according to claim 37, wherein the depositing of the ruthenium film includes supplying an inert gas including nitrogen and argon onto the substrate.

FIG. 1 (PRIOR ART)
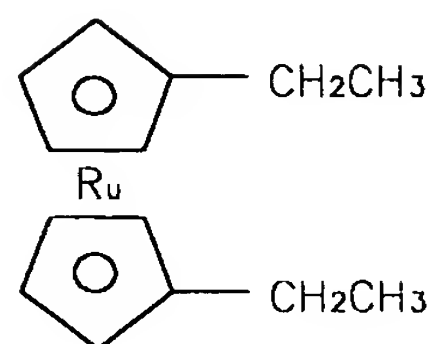
FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

Legend:
- Ru:0.6ccm, 02:100sccm
- Ru:0.6ccm, 02:54sccm
- Ru:0.6ccm, 02:8sccm
- Ru:1ccm, 02:54sccm
- Ru:0.2ccm, 02:54sccm

Y-axis: RESISTIVITY ($\mu\Omega \cdot cm$)
X-axis: TEMPERATURE (C°)

FIG. 8

Legend:
- Ru:0.6ccm, 02:100sccm
- Ru:0.6ccm, 02:54sccm
- Ru:0.6ccm, 02:8sccm
- Ru:1ccm, 02:54sccm
- Ru:0.2ccm, 02:54sccm

Y-axis: DEPOSITION RATE (Å/min)
X-axis: PRESSURE (Torr)

FIG. 9

Legend:
- Ru:0.6ccm, 02:100sccm
- Ru:0.6ccm, 02:54sccm
- Ru:0.6ccm, 02:8sccm
- Ru:1ccm, 02:54sccm
- Ru:0.2ccm, 02:54sccm

X-axis: PRESSURE (Torr)
Y-axis: RESISTIVITY ($\mu\Omega$.cm)

FIG. 10

Legend:
- RESISTIVITY
- DEPOSITION RATE
- STEP COVERAGE

X-axis: 02 SOURCE (sccm)
Y-axis: RESISTIVITY ($\mu\Omega$.cm) DEPOSITION RATE (Å/min) STEP COVERAGE (%)
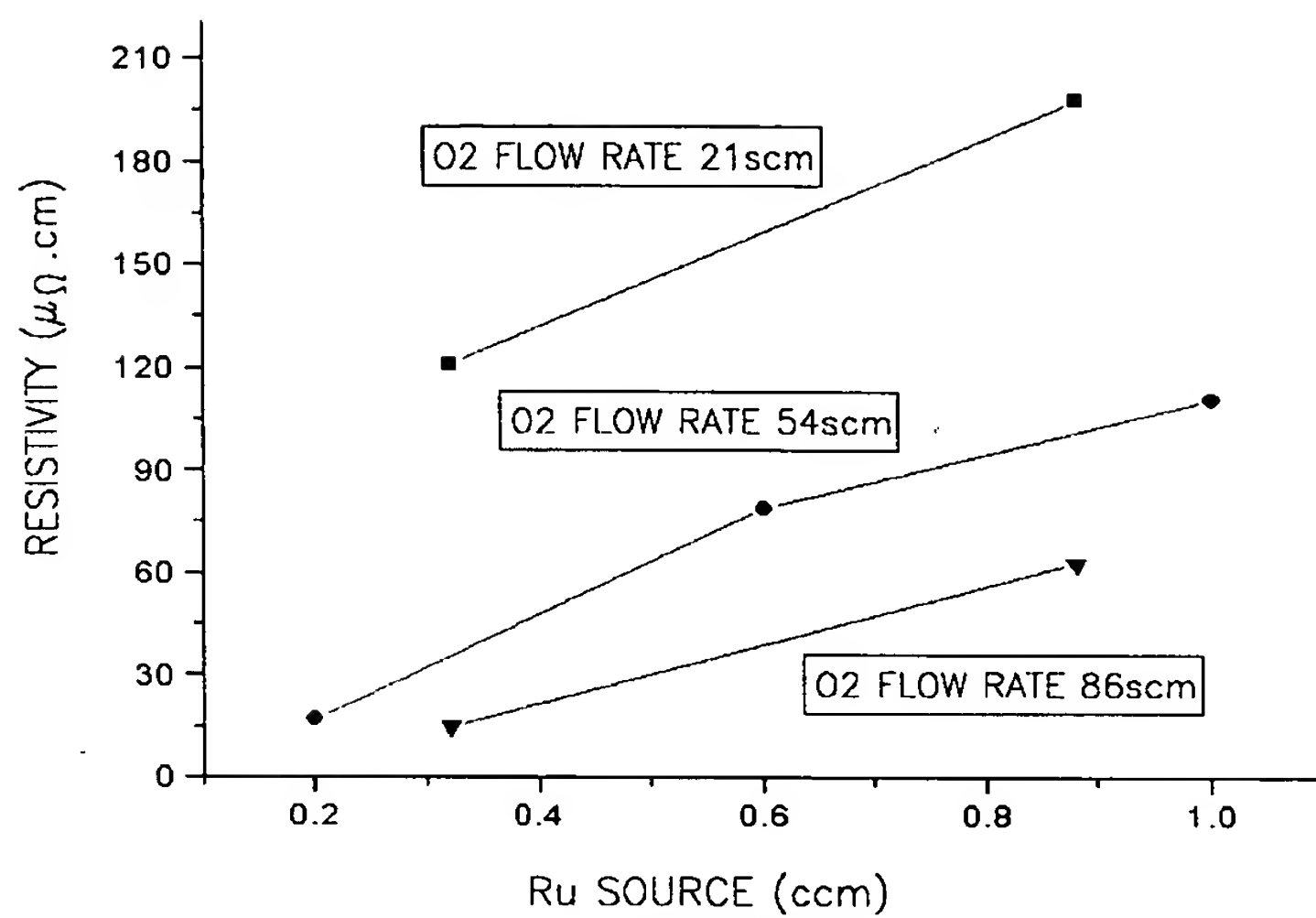
FIG. 11A

FIG. 11B

FIG. 11C

FIG. 12A
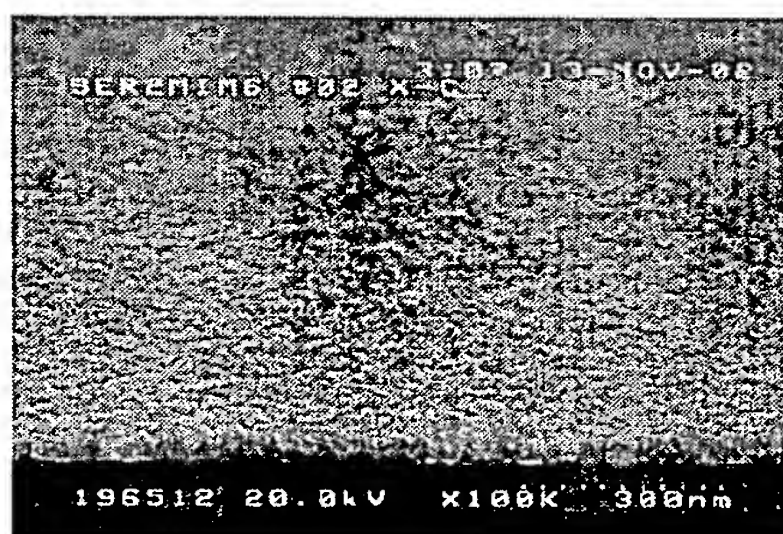
FIG. 12B
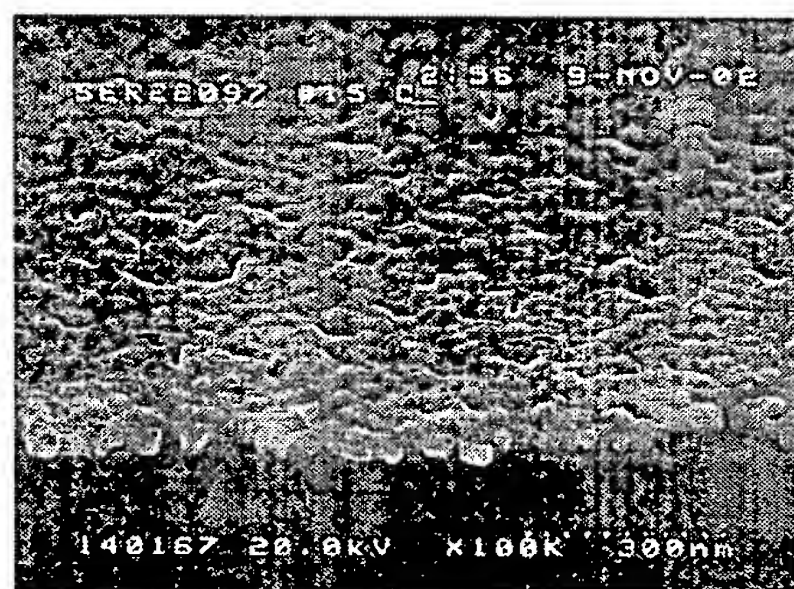
FIG. 12C
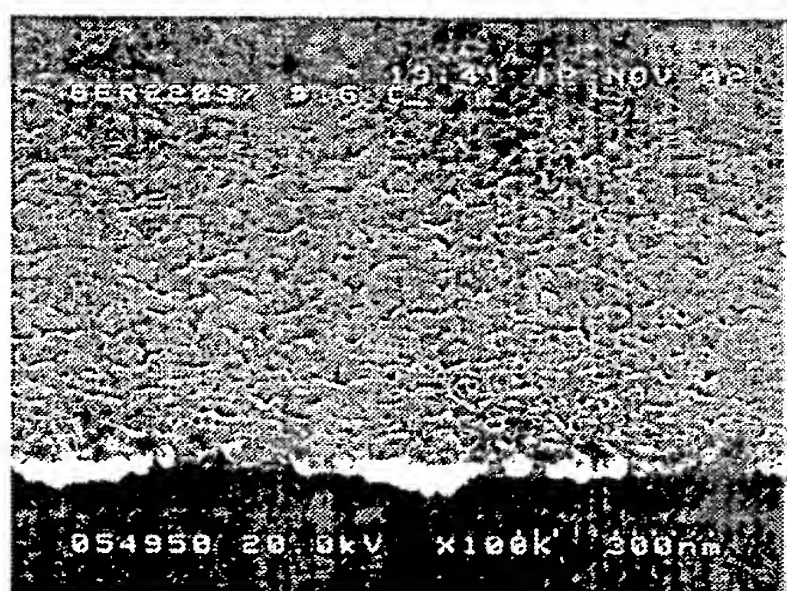
FIG. 13A
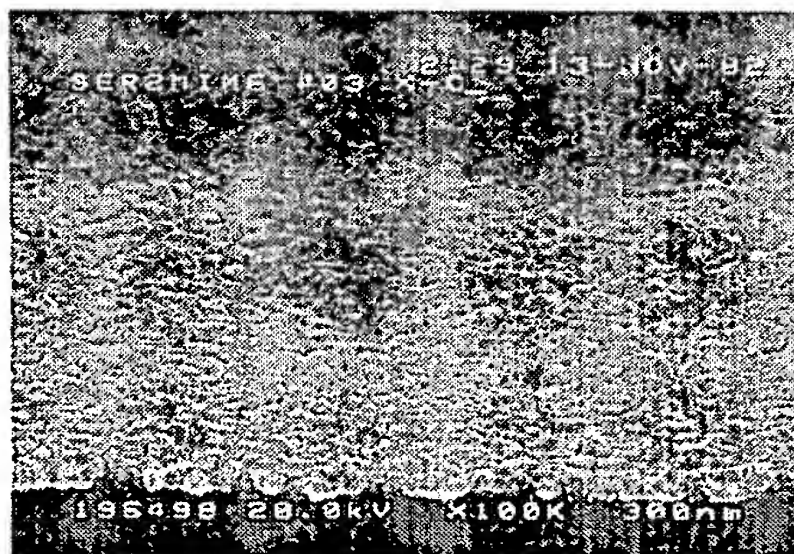
FIG. 13B

FIG. 13C

FIG. 14

FIG. 15

RESISTIVITY ($\mu\Omega$. cm) vs Ru SOURCE (ccm)

O2 FLOW RATE 21scm

O2 FLOW RATE 54scm

O2 FLOW RATE 86scm

FIG. 16

LEAKAGE CURRENT DENSITY (Å/cell) vs APPLIED VOLTAGE (V)

FIG. 17A

—220
—215
—218
—210
—205
—200

FIG. 17B

235
230 } 240
225
210
205
200